REACTIVITY OF SOME NITROGEN-CONTAINING COMPOUNDS AT SUPERCRITICAL WATER CONDITIONS

David M. Tiffany, Thomas J. Houser, Michael E. McCarville
and Michael E. Houghton

Department of Chemistry, Western Michigan University
Kalamazoo, MI   49008

INTRODUCTION

The possible use of supercritical fluid extraction (SFE) of coal to produce li-
quids has been attracting significant interest recently. The temperatures at which
SFE is generally carried out, about 400°C and above, will cause bond ruptures to oc-
cur in the coal structure. Thus, the extracting capability of the fluid is important
in terms of both the intermediate products, usually involatile at these temperatures,
as well as the original coal components. In addition, the fluid has the opportunity
to participate as a reactant at process conditions, which may yield extracts of dif-
ferent compositions that will be dependent on the fluid used.

Thermodynamic consideration of SFE leads to the prediction that the enhanced
solubility (volatility) of the solute has a very strong dependence on pressure (1).
The enhancement may be as large as a factor of 10^4 under very favorable conditions
(2). Thus, this method combines many of the advantages of distillation with those
of extraction. The general advantages of SFE as applied to coal processing have been
previously enumerated (1). Many of the reported studies in this area, using toluene
as the fluid, have originated in Great Britain. The influence of residence time,
temperature, and pressure on yield from the SFE of coal, using bench-scale and small
pilot plant units has been reported (3). Economic (4) and energy efficiency (5)
evaluations have indicated that SFE is competitive with most other coal conversion
processes. However, despite the strong interest in SFE there has been very little
reported on the basic chemistry that takes place during coal extraction by this tech-
nique.

One important function which coal processing can perform is the removal of het-
eroatoms to yield a cleaner product. In particular, the current program is concerned
with nitrogen removal from model compounds thought to be representative structures
found in coal. Studies have shown that quinoline type structures in coal liquefac-
tion are among the most difficult to remove (6); more recent studies on catalytic
hydrodenitrogenation of quinoline (7-9) have supported this assessment. Thus, exper-
iments have concentrated on examining the reactivities of quinoline and isoquinoline;
the reactivities of other compounds were studied briefly also. The selection of
water as the fluid was based on several properties, in addition to solvent expense,
which makes it suitable for the application of interest. Briefly, these properties
are: (a) Critical temperature, 374.2°C. Theoretical considerations have shown that
extract volatility enhancement is greatest when extraction is carried out near the
fluid critical temperature (10). (b) Temperature and pressure dependence of the di-
electric constant which will allow control of solvent properties (11). (c) High
reactivity with cyanide wastes to form ammonia (12). (d) Molecular polarity since
polar solvents exert a stronger depolymerizing action on coal than nonpolar ones and
also increase extraction rate (1). Experimental verification of the effectiveness of
water as an extracting fluid was indicated by the results reported in a study of sol-
vent effects in supercritical extraction of coal (13); water was more effective than
predicted from the theoretical calculations. The present paper discusses the results
obtained to date of the treatment of several nitrogen-containing compounds and alkyl-
benzenes with supercritical water, including some treatments using acid catalysts to
enhance reactivity. The expectation is to determine the least severe conditions at
which nitrogen can be removed from several types of molecular structures.

EXPERIMENTAL

The experiments were carried out in a small (47 cc) stainless steel, batch reactor which is not equipped with a pressure gauge or gas vent. The procedure was essentially the same for all experiments. The reactor was loaded with organic compounds (usually 2.00 mL for liquids, or 2.00 grams for solids, although a few quinoline experiments had different amounts), sufficient water was added to produce the desired pressure at reaction temperature as calculated from PVT data (14), catalyst was added as needed, the reactor purged with argon and bolted closed. The reactor was placed in the preheated furnace for the required reaction time. Initial experiments used an electric furnace but times to reach reaction temperature were found to be too long, which prompted a switch to a fluidized sand bath furnace, thus reducing heating times to reach critical temperature to about 15 minutes. Following reaction, the vessel was air cooled, opened, the reaction mixture removed and the water and organic layers filtered and separated. The reactor was washed with a portion of methylene chloride solvent and a second portion of solvent was used to extract the water layer. The organic layer was combined with the solvent portions and diluted to a standard volume of 25 mL with additional solvent.

The various phases were then measured quantitatively. The remaining volume of water and the mass of the char (defined as filterable solids) were determined. A few elemental analyses of the char were obtained. The ammonia produced and dissolved in the water layer was determined for some of the experiments with an ion specific electrode. The methylene chloride solution was examined gas chromatographically for products and extents of reaction. When a component was identified, standard solutions were prepared for quantitative determinations. Some components were confirmed using GC/MS analyses. There still was a significant fraction of product that remained dissolved and/or suspended in the solvent that did not show up on the chromatograms. This was termed the tar portion. Currently, this tar is being examined more closely.

RESULTS AND DISCUSSION

Isoquinoline

The results of the reaction of isoquinoline at supercritical water conditions and with water at these conditions are summarized in Table 1. The extents of reaction are significant but their dependence on time and pressure are not entirely unequivocal. The extents appear to level off at longer times and two increases in water pressure increased reaction extents while a third gave a small decrease. However, as with quinoline, the extents of reaction and the products found are different than those from the inert pyrolysis (15). The addition of zinc chloride appears to increase extents somewhat, as does the addition of tetralin or dihydroanthracene. The hydrogen transfer agents were consumed to a large extent also, but DA did not yield products that interfered with the reactant product chromatogram and estimates from a tetralin experiment run later allowed adjustments in the product peaks to produce the yields reported.

The results which are encouraging in terms of nitrogen removal are: (a) about 35 to 55 molar % of the converted reactant is in the form of desirable aromatics, benzene and alkyl benzenes, (b) most of the converted nitrogen appears as ammonia in the water phase and (c) the char is significantly reduced in nitrogen content as compared to the reactant. Other results to note are: (a) a rise in temperature appears to produce a relative increase in lighter molecular weight products as well as increasing extents of reaction, (b) the identifiable products are formed from heterocyclic ring rupture exclusively, thus leaving the homocyclic ring primarily intact, (this may not be true for the reactions leading to the tar/char formation) and (c) the effect of the hydrogen transfer agents indicate that prereduction, followed by water treatment may improve conversions.

It should also be noted that one experiment run at 450°C and for 48 hrs. without water showed less than 10% reaction (as compared to about 50% with water) and no mea-

surable product or char was found.

Quinoline

The results of the reaction of quinoline at supercritical water conditions are summarized in Table 2. The following observations can be made when comparing these with those from isoquinoline: quinoline is significantly less reactive, thus would require a catalytic agent, except at 500°C., and the product distribution is very different yielding a smaller fraction of identifiable products which also are primarily aromatic amines, aniline, toluidine and a small amount of quinaldine. The elemental analysis of one char sample did show a reduction in nitrogen content, but it was not as large as that found for the isoquinoline sample. One interesting observation is that two catalytic experiments at 400°C. gave essentially quantitative yields of ammonia. This will be investigated further including elemental analyses of tar and char. It is evident that there is a very large fraction of product in the form of unidentified tar.

Miscellaneous Compounds

The reactivities of several other compounds with supercritical water were examined and the results are summarized in Table 3. Benzonitrile and carbazole represent nitrogen-containing compounds with different functionalities than the quinolines and these exhibited the extremes in reactivity. Carbazole appears essentially unreacted at our conditions. Benzonitrile evidently hydrolyzed, followed by decarboxylation, very quickly and cleanly, no discoloration of the reaction mixture was observed.

Ethylbenzene and aniline were included because they were observed as products which may have further degradation. Ethylbenzene did react to a small extent, again very cleanly to predictable products, benzene and toluene. Aniline reacts to a larger extent yielding only two organic products in the chromatograms. The aniline results can be considered only qualitative at this point.

Because tetralin and dihydroanthracene were consumed in the reaction with isoquinoline, they were also examined. The tetralin was completely consumed, about half of which formed naphthalene; the other half undergoes ring rupture to produce benzene and at least four alkylbenzenes. Calibrations have not been determined as yet for the two products with the longer retention times than o-xylene, but mass spectra of these are consistent with a C_3-benzene and a C_4-benzene. A tetralin experiment run for 48 hours at 450°C. without water gave only 26% reaction, 58% of which formed naphthalene. The next larger product peak had a retention time consistent with those of n-butyl- or o-diethylbenzenes (which were not present in the water reaction product). The dihydroanthracene results are only qualitative but it appears that about half is converted to anthracene. In addition, at least five other products are formed in small amounts and these have retention times between those of naphthalene and anthracene.

CONCLUSIONS

It is evident from the results that supercritical water can be effective as an active reactant in the removal of nitrogen from several organic compounds as well as influencing the mechanism of hydrocarbon degradation. The effectiveness varies with molecular structure and there are indications that acidic catalysts, e.g., zinc chloride, can improve this effectiveness. Consideration of the extents of reaction shows that isoquinoline is much more susceptible to bond rupture than is quinoline. For isoquinoline, the product distribution shows a distinct preference to rupture the heterocyclic ring, but that rupture may occur with about equal probability between the 1-2 or 2-3 positions, followed by hydrolysis and decarboxylation. The 1-2 break would lead to o-xylene, the 2-3 to ethylbenzene, which are formed in about equal amounts. These products can then undergo further sidechain shortening or elimination.

Quinoline, on the other hand, does not react as readily and although the heterocyclic ring appears to be the preferential point of attack, the rupture is more probably between the 1-2 position than the 1-9 position. This fragment would not hydrolyze, but would produce alkyl anilines which could then further react. It was found that tar formation is far more probable with this reactant. It is interesting to note that supercritical water has a profound effect on both the extent of reaction (100 vs. 26%) and reaction mechanism of even the hydrocarbon, tetralin. Further mechanistic speculation will be deferred until additional data is obtained.

REFERENCES

1. N. Gangoli and G. Thodos, Ind. Eng. Chem., Prod. Res. Dev., 16, 208 (1977).

2. J.C. Whitehead and D.F. Williams, J. Inst. Fuel (London), 182 (1975).

3. J.C. Whitehead, "Development of a Process for the Supercritical Gas Extraction of Coal," 88th AIChE National Meeting, Philadelphia, June 1980.

4. R.R. Maddocks, J. Gibson and D.G. Williams, Chem. Eng. Prog., 75, 49 (1979).

5. F.R. Benn, "Production and Utilization of Synthetic Fuels - an Energy Economics Study," Halsted Press, New York, N.Y. 1981, pp. 19-36 and 175-201.

6. H.F. Silver, "Effects of Solvent Characteristics on Wyodak Coal Liquefaction," (FE-2367-5), April 1977.

7. J.F. Cocchetto and C.N. Satterfield, Ind. Eng. Chem. Process. Des. Dev., 20, 49 (1981).

8. C.N. Satterfield and J.F. Cocchetto, Ind. Eng. Chem. Process. Des. Dev., 20, 53 (1981).

9. L.J. Boucher, N.L. Holy and B.H. Davis," New Approaches in Coal Chemistry," Am. Chem. Soc., 1981, p. 319.

10. P.F.M. Paul and W.S. Wise, "The Principles of Gas Extraction," M & B Monographs CE/5, Mills & Boon (London) 1971.

11. E.U. Frank, Endeavour, 27 (101), 55 (1968).

12. Chementator, Dec. 25, 1972/Chem. Eng.; 20.

13. N.P. Vasilakos, J.M. Dobbs and A.S. Parisi, Preprint, Div. Fuel Chem., Am. Chem. Soc., 28 (4), 212 (1983).

14. J.H. Keenan, F.G. Keyes, P.G. Hill and J.G. Moore, "Thermodynamic Properties of Water Including Steam Tables," J. Wiley & Sons, New York, N.Y. (1969).

15. J.J. Madison and R.M. Roberts, Ind. Eng. Chem., 50, 237 (1958).

Table 1. Reaction of Water with Isoquinoline[a]

Temperature (C)	350	350	350	400	400	400	400	400	400	400	450	450	450	450	500	500
Pressure (psi)	2400	3640	3640	3870	3640	3870	3870	.3870	3870	3580	4680	4680c	4680c	4680	5200	4700
Density (g/cc)	0.255	0.170	0.170	0.213	0.170	0.213	0.213	0.213	0.213	0.106	0.170	0.170	0.170	0.170	0.213	0.128
Time (hour)	72	48	48	48	48	96	144	96	96	48	48	48	48	120	48	48
Catalyst	$ZnCl_2$	-	$ZnCl_2$	-	$ZnCl_2$	-	-	-	$ZnCl_2$	-	-	Tet	DA	-	-	-
(g)	(.08)	-	(.05)	-	(.05)	-	-	-	(.05)	-	-	(1.22)	(.50)	-	-	-
% Converted	34	18	54	30	54	50	50	50	57	50	42	93	58	85	81	70
Products (% of Converted Reactant)[b]																
Benzene	0	0	0	0	0	0	0	0	0.4	1.0	0.7	3.9	0	3.9	3.0	4.3
Toluene	0	5.0	6.3	10.7	8.8	14.2	16.6	15.2	10.5	17.0	24.0	16.7	9.0	21.3	21.1	16.6
Ethylbenzene	0.6	6.7	7.4	13.3	15.2	16.6	13.2	16.6	16.9	10.5	16.9	20.2	13.6	11.4	9.9	6.4
o-xylene	2.1	6.1	7.2	13.0	14.0	13.8	16.0	13.8	6.2	13.8	6.3	8.4	7.2	7.2	7.4	6.7
Ammonia	-	-	-	-	-	-	-	-	-	-	-	-	63	-	74	-
Water Recovered	-	99	92	98	98	98	98	98	99	90	99	99	90	84	90	87
Char	0	0	10.5	6.2	12.6	12.7	13.2	13.2	12.6	30.6	12.6	10.7	18.8	15.7	10.0	15.1d

a. An experiment run at 450C for 48 hours with no water gave greater than 90% reactant recovered and no products by GC or char.

b. Compounds are given as mole %, char as weight %. The remainder of the sample is tar and a few minor products - small peaks which appear to be aniline and toluidine were found but not measured.

c. These experiments were with added tetralin and dihydroanthracene. The extents of reaction are believed reliable but product distribution more uncertain because of consumption of hydrogen transfer agents.

d. Elemental analysis of this char gave the atom ratio $C_{21.7} H_{9.3} N_{1.0} O_{0.6}$.

60

Table 2. Reaction of Water with Quinoline

Temperature (C)	400					450					500
Pressure (psi)	3870	4020	4020	4660	4680	4680	5200	5200	5200	5200	5650
Density (g/cc)	0.213	0.255	0.255	0.426	0.170	0.170	0.213	0.213	0.213	0.213	0.170
Time (hour)	48	48	48	48	48	48	48	48	48	48	48
Catalyst	$ZnCl_2$	$AlCl_3$	$ZnCl_2$	-	$ZnCl_2$	$ZnCl_2$	-	$ZnCl_2$	$ZnCl_2$	$ZnCl_2$	-
(g)	(.05)	(.05)	(.05)	-	(.05)	(.10)	-	(.01)	(.05)	(.08)	-
% Converted	22	60	53	27	28	81	7	15	67	54	62
Products (% of Converted Reactant)[a]											
Benzene	0	0	0	0.7	0	0	0	0	0.6	0.2	3.9
Toluene	0.9	0	0	0	3.6	2.6	8.6	2.7	2.5	1.5	5.3
Ethylbenzene	2.7	0	0	0	1.8	1.0	8.6	4.0	1.2	1.5	1.9
o-xylene	2.7	0	0	0	0.4	0.5	4.3	4.7	0.9	0.9	0.2
Aniline	2.3	1.2	1.7	0	4.3	6.0	14.3	4.7	7.0	9.3	8.2
Toluidene	3.2	1.2	1.5	0	5.4	3.3	8.6	4.7	3.0	4.8	3.2
Ammonia	-	96	115.	-	-	-	-	-	-	-	-
Char	7.2	13.3	5.9	0	0	6.1	0	0	13.7	-	27b

(a) Compounds are given as mole %, char as weight %. The remainder of the sample is unidentified minor products or tar. Quinaldine was found but not measured.

(b) Elemental analysis of this char gave the atom ratio of $C_{13.9}H_{6.9}N_{1.0}O_{0.6}$.

61

Table 3. Reaction of Water with Other Compounds

Compound	Benzonitrile	Ethylbenzene	Tetralin[b]		DA[c]	Carbazole[d]	Aniline[e]	
Temperature (C)	400	450	450	450	450	450	450	450
Pressure (psi)	3640	5200	5200	5200	5200	5200	5200	5200
Density (g/cc)	0.170	0.213	0.213	0.213	0.213	0.213	0.213	0.213
Time (hour)	24	48	48	48	48	48	48	48
Catalyst	-	-	$ZnCl_2$	-	-	$ZnCl_2$	-	$ZnCl_2$
(g)	-	-	(.05)	-	-	(.05)	-	(.05)
% Reacted	100	10	100	100	>50	<15	21	74
Products[a]								
Benzene	95	22	1.5	1.5	0	0	s	s
Toluene	-	78	10	7.0	0	0	0	0
Ethylbenzene	-	-	13	8.9	0	0	0	0
Naphthalene	-	-	52	45	0	0	0	0
Anthracene	-	-	-	-	ℓ	0	0	0
Diphenylamine	-	-	-	-	-	-	ℓ	ℓ
Ammonia	-	-	-	-	-	-	66	59

a. Mole % of consumed reactant. No char found for any reactant.

b. Two other chromatographic peaks with retention times consistent with indan and methylindan were found but calibrations have not been made for these yet. The largest after that of naphthalene was the indan peak.

c. The dihydroanthracene chromatogram showed about six products, all having longer retention times than naphthalene but shorter than anthracene which was by far the largest, another was benzophenone but the others have not been identified as yet.

d. Carbazole appeared close to zero % reacted.

e. Due to chromatogram anomalies, the extents of these reactions are more uncertain. The only significant organic products in the chromatograms are the two reported in relatively small and large amounts. The s and ℓ indicate small and large product peaks respectively.

62

NOVEL LIQUEFACTION SOLVENT: H_2O-H_2S

Virgil I. Stenberg, Robert D. Hei, Philip G. Sweeny, Jan Nowok

Department of Chemistry, University of North Dakota
Box 7185 University Station, Grand Forks, ND 58202

Warrack G. Willson

University of North Dakota Energy Research Center
University of North Dakota, Grand Forks, ND 58202

INTRODUCTION

The liquefaction solvent has two roles to fulfill: (1) a slurrying liquid for the coal which enables slurry compression into a continuous flow reactor, and (2) a hydrogen shuttler which enables the transfer of hydrogen atoms from H_2 or synthesis gas to the coal molecules. Additionally, the solvent serves as a medium for reducing gas and coal product dissolution.

We now wish to describe the use of H_2O-H_2S as a substitute for organic slurrying solvents. The philosophy for doing so is that the water fulfills the role of the slurrying liquid and H_2S is the hydrogen atom donor. Since the first bond dissociation energy of water is 118 kcal/mole, rarely, if at all, would it be expected to react with carbon radicals. On the other hand, H_2S has the first bond dissociation energy of 93 kcal/mole and the second of 83 kcal/mole making it a good but not excellent hydrogen atom donor to carbon radicals (reaction 1). At the higher temperatures of conventional coal liquefaction reactors the thermodynamics would probably be more favorable. Reaction 2 has proven to be rapid at coal liquefaction temperatures and is

$$2R^{\cdot} + H_2S \rightarrow 2RH + S \qquad\qquad (1)$$

$$S + H_2 \rightarrow H_2S \qquad\qquad (2)$$
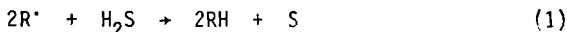
perhaps the principal advantage of H_2S over an organic solvent. The corresponding reaction for the organic solvent is usually slow. In organic liquefaction solvents, H_2S is known to enhance liquefaction yields, and it has been used for both coal and organic model compound reactions.[1]

Water becomes supercritical at 374°C and its supercritical state has the potential of influencing the liquefaction processes in several ways: it (1) becomes a fine solvent for hydrocarbons[3] (Fig. 1), (2) loses much of its ability to dissolve inorganic material (Fig. 2)[3], (3) adds to the reaction pressure, and (4) becomes more ionic (acidic and basic) since the ionization constant increases by ca. 3 powers of ten (Fig. 3).[4] If water is to be substituted for an organic slurrying liquid, the increase in reaction pressure
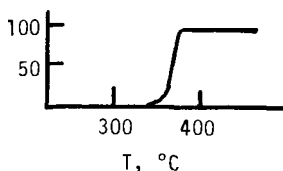
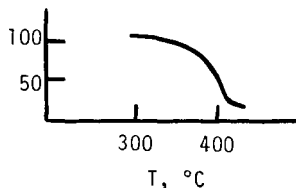

Fig. 1. Hydrocarbon solubility (wt %) in water

Fig. 2. Inorganic solubility (wt %) in water

(to ca. 5,000 psi) must be tolerated. Therefore, one must insist there be compensating factors for this pressure increase which more than make up for the cost of increased operating pressures. Batch autoclave data now indicate this is so. Indeed, water appears to have a positive effect on liquefaction yields in addition to its role as a slurrying liquid.
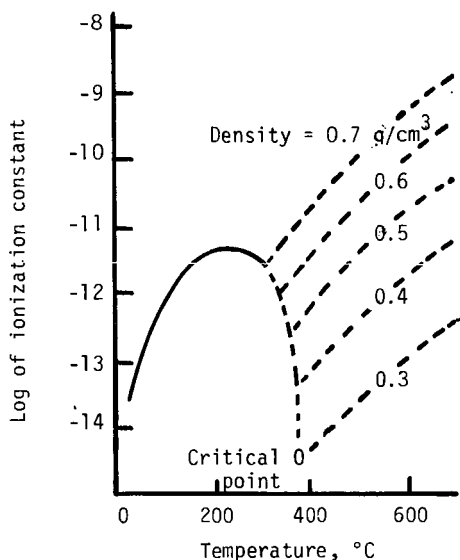

Fig. 3. Ionization constant of water in high-temperature fluids of various densities. The solid line is the experimentally determined curve for liquid water under its own vapor pressure. The estimated extrapolation of the curve to the critical point is shown as a dashed line. The other dashed lines shown calculated values of the constant for single-phase fluid water under sufficient pressure to maintain the indicated densities.

RESULTS AND DISCUSSION

The data of Table 1 compare the H_2O-H_2S results along with those using (1) a petroleum-coal based organic solvent, anthracene oil (AO4) together with a solvent refined coal middle distillate from the demonstration plant at Tacoma, Washington (SRCMD) and (2) dihydropyrene (DHP), a reputedly excellent hydrogen donor solvent. Three ranks of coals are represented in the data.

Water with synthesis gas outperform AO4-SRCMD with synthesis gas for the conversion of two coal samples into volatile materials at the conditions used, cf. runs 5 vs. 7 and 14 vs. 16. The presence of a small amount of H_2S enhances the as-defined yields whether in water, cf. runs 1 vs. 2, 7 vs. 8, 16 vs. 17, 21 vs. 22, 26 vs. 27 and 31 vs. 32 or in an organic solvent, cf. 5 vs. 6, 12

vs. 13, 14 vs. 15, 19 vs. 20, 24 vs. 25 and 34 vs. 35. The reactions which had the temperature programmed from 300°C to 500°C using H_2O-H_2S and synthesis gas gave the best of the aqueous-H_2S conversion yields, cf. runs 8 vs. 9, 17 vs. 18, 22 vs. 23, 27 vs. 28 and 32 vs. 33. Synthesis gas is superior to pure H_2 (980 psig), cf. runs 3 vs. 5 and 12 vs. 14.

The philosophy behind the temperature programmed reactions was the belief that the thermally produced, coal-derived radicals would be formed in a more controllable fashion, i.e., in a more steady, slower rate, within the coal-water slurry than with a sudden thermal jump to a preselected reaction temperature. The latter is assumed to momentarily deplete the hydrogen donor capacity of the solvent system at least in the vacinity of the thermal reaction events. In the case where water is the principal solvent, the hydrogen donor capacity is the H_2S concentration. The consequence of this depletion is the occurrence of retrograde reactions which result in lower conversions.

The dihydrophenanthrene (DHP) runs gave better conversions than either water or AO4-SRCMD given otherwise the same experimental conditions. However, DHP decomposes to the extent of 11% at 420°C at 30 minutes, and the non gaseous products are solids rather than liquids as they are with the water runs. The water runs were the easiest to separate from the product slurry. The distillation was complete in ca. 3 hours with the water runs whereas it took from 5-7 hours to get to constant weight with the organic solvent-based runs. The oil separated by gravity from the water in the water based run distillates.

In summary, the H_2O-H_2S solvent runs with various ranks of coals give respectable yields of total volatile materials at 420°C and with temperature programming the reactor from 300° to 500°C, the yields were as good if not better than using one of the best of hydrogen donor model compound solvents. The H_2S concentration the programing rates or ranges have not been optimized.

ACKNOWLEDGMENT

REFERENCES
1. (a) Stenberg, V.I.; Baltisberger, R.J.; Ogawa, T.; Raman, K., and Woolsey, N.F., Hydrogen Sulfide Catalysis of Low Rank Coal Liquefaction, ACS Fuel Division Preprints, 1982, 27(3-4), 22. (b) Stenberg, V.I.; Raman, K.; Srinivas, V.R.; Baltisberger, R.J., and Woolsey, N.F., H_2S as a Promotor for the Water Gas Shift Reaction, Angew. Chemie, Int. Ed., Engl., 1982, 21(8), 619. (c) Sondreal, E.A.; Wilson, W.G., and Stenberg, V.I., Mechanisms Leading to Process Improvements in Lignite Liquefaction Using CO and H_2S, Fuel, 1982, 61, 926.
2. (a) Gatsis, J.G., U.S. Patent No. 3 503 863 (1970). (b) Bearden, R., Jr. and Albridge, C.L., U.S. Patents Nos. 4 077 867 (1978), 4 094 765 (1978) and 4 149 959 (1979). (c) Lambert, J.M., Jr., Fuel, 1982, 61, 777. (d) Abdel-Baset, M.B. and Ratcliffe, C.T., Preprints. Div. of Fuel Chemistry, Amer. Chem. Soc., 1979, 25(1), 1. (e) Baldwin, R.M. and Viciguerra, S., Fuel, 1983, 62, 498. (f) Okutani, T., Yokoyama, S. and Maekawa, Y., Ind. Eng. Chem. Process Des. Dev., 1983, 22, 306.
3. (a) Josephson, J., Environ. Sci. Technol., 1982, 16(10), 548A. (b) Mackay, M.E., and Paulaitis, Ind. Eng. Chem. Fundam., 1979, 182), 149. (c) Johnston, K.P., Ziger, D.H., and Eckert, C.A., ibid, 1982, 21, 191. (d) Procaccia, I., and Gitterman, M., AIChE Journal, 1983, 29(4), 686. (e) Johnston, K.P., and Eckert, C.A., ibid., 1981, 27(5), 774.
4. Krauskopf, K.B., "Introduction to Geochemistry", McGraw-Hill Book Company, New York, NY, p. 496.

Table 1. The Conversion of Coals in H_2O-H_2S and AO4-SRCMD

	Lignites	Reducing gases	Temperature, °C	Sovent	Conversion, %
1	Indianhead (Zap I)	CO-H_2	420	H_2O	37.4
2	Indianhead	H_2S-CO-H_2	420	H_2O	42.8
3	Big Brown (BB1)	H_2	420	AO4-SRCMD	35.2
4	Big Brown	H_2S-H_2	420	AO4-SRCMD	35.3
5	Big Brown	CO-H_2	420	AO4-SRCMD	42.5
6	Big Brown	H_2S-CO-H_2	420	AO4-SRCMD	48.1
7	Big Brown	CO-H_2	420	H_2O	43.7 ± 2.0
8	Big Brown	H_2S-CO-H_2	420	H_2O	48.9 ± 1.2
9	Big Brown	H_2S-CO-H_2	300-500	H_2O	71.0
10	Big Brown	CO-H_2	420	DHP	50.7 ± 4.4
11	Big Brown	H_2S-CO-H_2	420	DHP	65.3 ± 3.5
12	Beulah (B3)	H_2	420	AO4-SRCMD	22.2
13	Beulah	H_2S-H_2	420	AO4-SRCMD	29.3
14	Beulah	CO-H_2	420	AO4-SRCMD	30.1
15	Beulah	H_2S-CO-H_2	420	AO4-SRCMD	40.5
16	Beulah	CO-H_2	420	H_2O	33.8 ± 1.0
17	Beulah	H_2S-CO-H_2	420	H_2O	36.8 ± 0.3
18	Beulah	H_2S-CO-H_2	300-500	H_2O	51.6 ± 1.1
19	Beulah	CO-H_2	420	DHP	46.6
20	Beulah	H_2S-CO-H_2	420	DHP	53.3 ± 3.0

Subbituminous coals

		Reducing gases	Temperature, °C	Sovent	Conversion, %
21	Decker (DEC 1)	CO-H_2	420	H_2O	38.6 ± 0.4
22	Decker	H_2S-CO-H_2	420	H_2O	40.6 ± 1.5
23	Decker	H_2S-CO-H_2	300-500	H_2O	52.3 ± 0.7
24	Decker	CO-H_2	420	DHP	48.4
25	Decker	H_2S-CO-H_2	420	DHP	60.2 ± 8.0
26	Absaloka (ABS 1)	CO-H_2	420	H_2O	29.6 ± 0.3
27	Absaloka	H_2S-CO-H_2	420	H_2O	34.1 ± 1.1
28	Absaloka	H_2S-CO-H_2	300-500	H_2O	51.0 ± 0.7
29	Absaloka	CO-H_2	420	DHP	N.A.
30	Absaloka	H_2S-CO-H_2	420	DHP	49.6 ± 3.5

Bituminous coals

		Reducing gases	Temperature, °C	Sovent	Conversion, %
31	Powhattan (POW 1)	CO-H_2	420	H_2O	24.7 ± 0.4
32	Powhattan	H_2S-CO-H_2	420	H_2O	30.5 ± 0.8
33	Powhattan	H_2S-CO-H_2	300-500	H_2O	41.9 ± 0.7
34	Powhattan	CO-H_2	420	DHP	43.5
35	Powhattan	H_2S-CO-H_2	420	DHP	51.6 ± 3.5

The experimental conditions are: reaction time, 1 hour; H_2S, 250 psig; CO, 490 psig; H_2, 490 psig; coal, 1 gram; and water, 1 gram. When H_2 alone was used, its pressure was 980 psig. The conversion yields were determined by distilling the volatile material (gases and liquids) from the reactor contents at 250°C at 1 Torr for 5 hours (H_2O) and 7 hours (AO4-SRCMD). The coal samples are cited from the mine site: Indianhead from the Indianhead Mine at Zap, North Dakota; Big Brown from the Big Brown Mine at Fairfield, Texas; Beulah from the South Beulah Mine, Beulah, North Dakota; Decker from the Decker Mine at Big Horn, Montana; Absaloka from the Absaloka Mine at Sarpy Creek, Montana; and Powhattan from the Powhattan Mine at Belmont, Ohio.

LOW SEVERITY CATALYTIC HYDROGENATION OF COALS IN THE ABSENCE OF SOLVENT

P. Stansberry, M-T. Terrer, F. J. Derbyshire, and D. H. Finseth*

Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA   16802

*U.S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA   15236

Introduction

Historically, models of coal structure have been developed on the premise that its principal characteristics can be attributed to those of a complex solid phase. Attempts to describe and portray this phase have focused on embodying measured compositional parameters into an 'average' molecule which presents a statistical representation of the whole molecular assembly. The value of such an approach is very limited particularly in its ability to describe behavioral characteristics. Furthermore, it does not take account of the existence of comparatively low molecular weight extractable liquids which are present in all except anthracitic coals (1).

In bituminous coals, the chloroform soluble materials have been shown to directly influence coal fluid properties (2-4). The role of the 'bitumens' has been suggested to be that of solvating and hydrogen-donating agents for the remainder of the coal substance (2). By analogy, it has been proposed that extractable coal liquids can provide a similar function during coal liquefaction (5). Experiments have shown that the extraction of bituminous and subbituminous coals in chloroform prior to liquefaction adversely influences the net liquefaction yield (6).

At moderate temperatures only a small proportion of coal may be extractable in solvents such as chloroform. However, it has long been recognized that by preheating the coal up to temperatures of 400°C and above, the yield can be increased several fold (2,7-8). Brown and Waters (2) concluded that the normal yield of extract is related to the accessibility of the pores to solvent, which is enhanced by preheating (swelling). Similarly, it has been found that the yields of alkanes present in benzene/ethanol solvent extracts was higher by 8-10 times in the liquefaction products of the same coals, although the distribution of the various species was very similar in both cases. It was concluded that the increased yield of alkanes on liquefaction was due to their liberation from regions of the structure hitherto inaccessible to solvent (9).

The work of Vahrman (10) has shown that in the Soxhlet extraction of coals extended for several hundred hours, the quantity of extract progressively increases, albeit at very low rates, and ultimately approaches that of the tar produced in low temperature (450°) pyrolysis. These findings are consistent with more recent suggestions to the effect that proportion of coal which is potentially extractable is much larger than is generally assumed but that it is not readily available due its being contained in closed or restricted porosity (11).

There are at least two possible sources of extractable or trapped liquids; by reactions during coalification leading to the formation and accumulation of lower molecular weight material (2); by physical entrapment of relatively unmodified components of plant origin (9,12-14). The presence of these materials in the

coal mass and their influence on its properties have promoted a number of suggestions concerning coal structure (1,2) which have been revitalized in recent years (15-17). Essentially coal is considered to comprise a relatively rigidly bonded three dimensional network which acts as a host for lower molecular weight species contained in both open and closed or partially closed pores. In effect, the structural model is that of a multicomponent system which, in the light of present knowledge, appears to be a more consistent and realistic basis for coal research than the earlier single phase concepts.

With this background, research investigations have been initiated to examine the low temperature ($\leq 400^\circ$C) catalytic hydrogenation of coals. The general objectives are to determine if it is possible to increase the yield of extractable liquids through the breakdown or modification of the network under mild hydrogenative conditions. Through, so doing, it is hoped i) to derive information about the structures and interactions of the 'network' and 'mobile' phases and ii) to ascertain the influence of such a pretreatment upon the behavior of coal in subsequent reactions. Earlier research has shown that low temperature chemical reduction of coals (treatment with a solution of lithium in ethylamine) can increase the H/C ratio and solubility in pyridine (18).

The approach which has been adopted follows the work of Hawk and Hitsehue (19) and Weller (20) who investigated catalytic coal hydrogenation in the absence of solvent in order to reduce the number of variables in the system and the problems of interpretation. The principal difference in the studies reported here, compared to the earlier work, is that reactions have been conducted at substantially lower temperatures and pressures.

Experimental

Coal Preparation

Samples of a bituminous coal were obtained in undried 1/2" lump form from The Pennsylvania State University Coal Sample Bank. The coals were ground, without drying to minus 800x10^{-6} m in a glove box which was first purged and maintained under pressure using a flow of oxygen-free nitrogen. The total ground product was riffled and then divided into approximately 20 gram lots which were sealed into vials while still in the glove box. The origin and analysis of the ground coals are summarized in Table 1.

The molybdenum catalyst used in these experiments was impregnated onto the coals using an aqueous solution of ammonium hepta molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (supplied by courtesy of Climax Molybdenum, Co.). The procedure was to mix the prerequisite quantity of the molybdenum salt with the coal following which sufficient distilled water was added to form a thick slurry which was stirred for 30 minutes at room temperature. The excess water was removed by vacuum at room temperature overnight. (It was estimated that by this technique more than 98% wt of catalyst was retained on the coal.)

Reaction and Product Workings

Reactions were carried out using standard tubing bombs (20 cc capacity) constructed out of 316 stainless steel which were loaded with approximately 5 g of sample. The bombs were first purged of air several times with nitrogen and, if required, purged of nitrogen and sealed with the reactant gas to a cold pressure of 1000 psig. The bombs were heated by immersion in a preheated fluidized sandbath heater which rapidly raised the contents of the bomb to reaction temperature. Agitation was provided by oscillating the bomb through a vertical displacement of 5 cm at a frequency of 50 sec^{-1}. At the end of the reaction period, the bomb was

removed from the sandbath and quenched by immersion in water.

The excess pressure in the bomb was released by venting at room temperature
during which time gas samples were collected for analysis. The reactor contents
were completely removed to a predried ceramic Soxhlet thimble using chloroform as
wash solvent. Soxhlet extractions were then carried out for 12 hours in boiling
chloroform under a protective blanket of nitrogen. The resulting residue was dried
in vacuo at $110^{o}C$ for 12 hours to remove remaining solvent.

The chloroform extracts were filtered (Whatman 42 filter paper) under a
nitrogen blanket and the excess chloroform removed on a rotary evaporator at
$40^{o}C$. The resulting product was then further dried in vacuo for 1 hour at
$110^{o}C$. The residual and extract products were sealed under nitrogen and stored
under refrigerated conditions.

The total yields of chloroform soluble extract and gases were calculated from
the mass of dried chloroform insoluble residue and reported as a percentage of dmmf
coal. In those cases where catalyst had been added, the assumption was made that
the molybdenum in the residue had been converted to a 50-50 mixture of MoO_3 and
MoS_2. This assumption requires verification but any resulting inaccuracy does
not affect the general trend shown in the data. The reproducibility of the total
yields was found to be within 2%.

Analytical

The chloroform soluble extracts, the insoluble residues and nonextracted coals
were analyzed for elemental composition. The extracts were also analyzed by ^{1}H
n.m.r. spectroscopy (using pyridine as solvent) and by high resolution mass
spectrometry (KRATOS M-50 spectrometer, resolution 1:30,000). The mass
spectrometric method employed direct probe sample introduction which allows analysis
of materials which are volatilized at $350^{o}C$ and a pressure of 10^{-6} mm of
mercury.

The parent coals and nonextracted, reacted samples were analyzed by ^{13}C
n.m.r. using two independent methods to determine differences in aromaticity;
cross-polar magic angle spinning and the Bloch decay technique.[21]

Results and Discussion

Extract Yields

The total yields of chloroform extracted liquids and gases obtained under
different reaction conditions are shown in Table 2 and are presented in Figure 1.
It can be seen that the extract yield obtained in nitrogen increases with
temperature from 0.9% at $61^{o}C$ to a value of 9.2% at $400^{o}C$. The effects of
heating on extract yield are consistent with those reported previously (1,2,7,8) and
the value at $400^{o}C$ is of the same order as has been measured for coals of
similar rank (2).

More notably, at temperatures above about $325^{o}C$, the total yield is
increased to some degree by the presence of hydrogen gas and more appreciably by the
combination of hydrogen and impregnated catalyst. In the latter case, the yield at
$400^{o}C$ amounted to 43.1% of dmmf coal which is more than a factor of two higher
than obtained in hydrogen alone and over four times that in nitrogen. Accurate
figures for the gas make are not yet available although from preliminary estimates
the quantity does not appear to be higher than about 5% dmmf coal at the maximum
total yield measured. Consequently, it can be seen that by catalytic hydrogenation
a substantial proportion of the coal substance has been rendered soluble and

TABLE 1

COAL ANALYSIS

Coal Identification

Rank	Bituminous HVA
Sample Band I.D.	PSOC 1266
Seam	Ohio #5 (Lower Kittanning)
Mine	East Fairfield C

Analysis

Moisture % a.r.	3.36
Mineral Matter % m.f.*	6.09

Elemental Analysis (dmmf)

C	83.20
H	4.97
O (by diff)	8.64
N	2.06
S	1.35
H/C atomic ratio	0.76

*by low temperature ashing

TABLE 2

TOTAL YIELDS (CHLOROFORM SOLUBLES AND GASES) FROM BITUMINOUS COAL
REACTED FOR 1 h, 1000 psig GAS (COLD)

Reaction Temperature, °C	Yield % dmmf+	
	Noncatalyzed	Catalyzed*
250	0.9	0.3
300	1.2	1.3
350	6.3	9.2
400	19.3	43.1

+Yields are the average of at least two results. Estimated error ±1%.

*5% Mo on a.r. coal added as ammonium hepta molybdate.

70

extractable in chloroform. The lesser improvement in yield found in hydrogen alone may be attributable to catalysis by dispersed mineral matter.

From these data it is not possible to ascertain whether the chloroform soluble materials realized under hydrogenative conditions are derived solely from the more efficient liberation of trapped species or whether there is some accompanying decomposition of the 'network.' Nevertheless, the high yields obtained with impregnated catalyst suggest that a proportion of the extractable products may be produced through reactions which involve breaking relatively strong chemical bonds.

Coal and Extract Composition

The coal aromaticities measured by ^{13}C n.m.r. are shown in Table 3. The results obtained by the two methods differ significantly in absolute terms, reasons for which are currently being investigated. The differences are, however, systematic and depict the same relative changes in f_a, which show that under both sets of reaction conditions the aromaticity increases. In the presence of catalyst the extent of aromatization is reduced but the net chemical reactions evidently involve dehydrogenation rather than hydrogenation.

The hydrogen contents and the H/C ratios of the coals and residues, Table 4, are consistent with the ^{13}C n.m.r. analyses. The results for the chloroform soluble extracts do not reflect the same trend, the hydrogen content of the extracts derived following reaction being similar to or higher than that from the parent coal. In the absence of gas analyses, it is difficult to draw any inference from these data, although it is noteworthy that the hydrogen content of the extracts is little influenced by the substantial changes in yield.

The role of the added catalyst is not at all clear. Its addition results in a two-fold increase in an extractable material while apparently there is only a small effect on net hydrogenation.

Further compositional analyses of the extracts were undertaken to attempt to elucidate the function of the catalyst and the origins of the additional chloroform soluble liquids. The hydrogen type distributions by ^1H n.m.r. of extracts, derived from hydrogenative reactions in the presence and absence of added catalyst, were found to be virtually indistinguishable, Table 5.

A comparison of the distribution of hydrocarbon fractions of these same samples obtained by high resolution mass spectrometry (HRMS) and subsequent data reduction is shown in Figure 2. The format for this figure is simply a plot of ion intensity vs Z number class (C_xH_{2x-z}) with each Z number class ordered by carbon number. (Thus, benzenes contribute to Z=6 napthalenes to Z=12 phenanthrenes to Z=18 and pyrenes to Z=22.) The yield of hydrocarbons (as a fraction of total extract) was approximately the same for the two extracts (32% for catalyzed, 35% noncatalyzed) and the similarity of the HRMS profiles indicates that the distribution and composition of the hydocarbons is also very similar. This close correspondence of HRMS profiles was also observed for other compound classes in the extracts ($C_xH_yO_2$, C_xH_yO, C_xH_yN).

A number of minor differences were detected in all of the profiles but it is not yet known if they are reproducible or significant. A further and possibly important distinction was that in the monoxygenate profile (C_xH_yO) the extract from the catalyzed reaction showed a higher concentration of monoaromatic phenols. Examination by dispersive infrared spectrometry confirmed that this extract contained a measurably higher concentration of phenolic -OH groups. This particular phenomenon which has been noted in earlier studies of low temperature coal reduction (18) is the subject of continuing investigation.

TABLE 3

AROMATICITIES OF NONEXTRACTED COALS BY ^{13}C n.m.r.

	Parent Coal	Reaction at 400°C, 1 h, 1000 psig H_2 (cold)	
		No Added Catalyst	Mo Impregnated
f_a (CP-MAS)	0.71	0.78	0.74
f_a (Block Decay)	0.75	0.84	0.79

TABLE 4

HYDROGEN CONTENT AND H/C ATOMIC RATIO OF COALS, EXTRACTS AND RESIDUES

Sample		Parent Coal	Reaction 400°C, 1 h, 1000 psig H_2 (cold)	
			No Added Catalyst	Mo Impregnated
Coal	H wt% dmmf	4.97	4.51	5.06
	H/C Atomic ratio	0.72	0.65	0.71
Residue	H % dmmf	4.86	4.00	4.61
	H/C atomic ratio	0.71	0.58	0.63
Extract	H % dmmf	6.52	7.25	6.95
	H/C atomic ratio	1.01	1.05	1.00

TABLE 5

HYDROGEN TYPE DISTRIBUTION OF CHLOROFORM SOLUBLE EXTRACTS BY ^{1}H n.m.r.
(coal reacted at 400°C, 1000 psig H_2)

Sample	H_α	H_β	H_γ	H_{Ar}
No added catalyst	0.36	0.25	0.06	0.32
Mo impregnated	0.34	0.24	0.07	0.30

Overall (and excepting the possible production of phenols) although the catalyst has been found to have a major influence upon the release and/or production of chloroform soluble material, the available compositional information indicates that its mechanism is unusually subtle. The additionally extractable liquids, whether originally trapped or derived from the 'network' are very similar in structure to those generated in the absence of catalyst.

Acknowledgements

References

1. van Krevelen, D. W., Fuel 1976, 44, 229.

2. Brown, H. R. and Waters, P. L., Fuel 1966, 45, 17-39.

3. van Krevelen, D. W., "Coal," Elsevier Publishing Co., New York, 1961.

4. Walters, J. G., Shultz, J. L., and Glaenzer, J. A., U.S. Bureau of Mines Report of Investigations G973, 1967.

5. Neavel, R. C., "Coal Science," Volume 1, Academic Press, New York, 1982.

6. Larsen, J. W., Sams, T. L., and Rodgers, B. R., Fuel 1980, 59, 667-668.

7. Illingworth, S. R., J. Soc. Chem. Ind. 1920, 39, 111-118.

8. Dryden, I. G. C. and Pankhurst, K. S., Fuel 1955, 34, 363-366.

9. Youtcheff, J. S., Jr., Ph.D. Thesis, The Pennsylvania State University, 1983.

10. Vahrman, M., "Chemistry in Britain," 1972, 8, 16-24.

11. Jurkiewicz, A., Marzec, A., and Pislewski, N., Fuel 1982, 61, 647-650.

12. Baset, Z. H., Pancirov, R. J., and Ashe, T. R. "Advances in Organic Geochemistry," Ed. A. G. Douglas and J. R. Maxwell, Pergaman, Oxford, 619-630.

13. Snape, C. E., Stokes, B. J., and Bartle, K. D., Fuel 1981, 60, 903-908.

14. Calkins, W. H., ACS Division of Fuel Chemistry, Preprints, Vol. 28, No. 5, 85-105.

15. Larsen, J. W., "Chemistry and Physics of Coal Utilization" (Ed. B. R. Cooper and L. Petrakis) American Institute of Physics, New York, 1980, pp. 1-27.

16. Lucht, L. M. and Peppas, N. A., "Chemistry and Physics of Coal Utilization" (Ed. B. R. Cooper and L. Petrakis) American Institute of Physics, New York, 1980, pp. 28-48.

17. Lucht, L. M. and Peppas, N. A., "New Approaches in Coal Chemistry," Amer. Chem.

Soc. Symp. Series 169, 1981, 43-59.

18. Given, P. H., Lupton, V., and Peover, M. E., Proceedings of the Conference on
     Science in the Use of Coal, Institute of Fuel, Sheffield, U.K., 1958.

19. Hawk, C. O. and Hiteshue, R. W., U. S. Bureau of Mines Bulletin 622, 1965.

20. Weller, S. W. (1982), Coal Liquefaction with Molybdenum Catalysts, IV
     Internat. Conf. on Chem. and Uses of Molybdenum, Golden, Colorado.

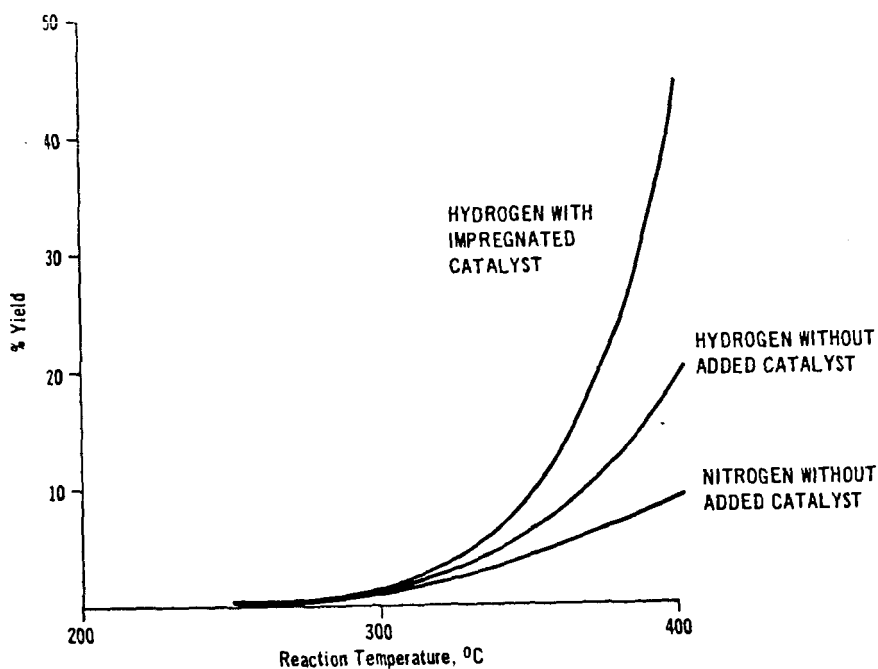21. Reinhold, Michael Bruker Instruments, Inc. Personal communication.

Figure 1. YIELD OF CHLOROFORM SOLUBLE LIQUIDS AND GASES AS A FUNCTION
           OF REACTION TEMPERATURE
           (Bituminous coal, 5% M_0 loading on as-received coal, reaction 1h, 1000 psig cold
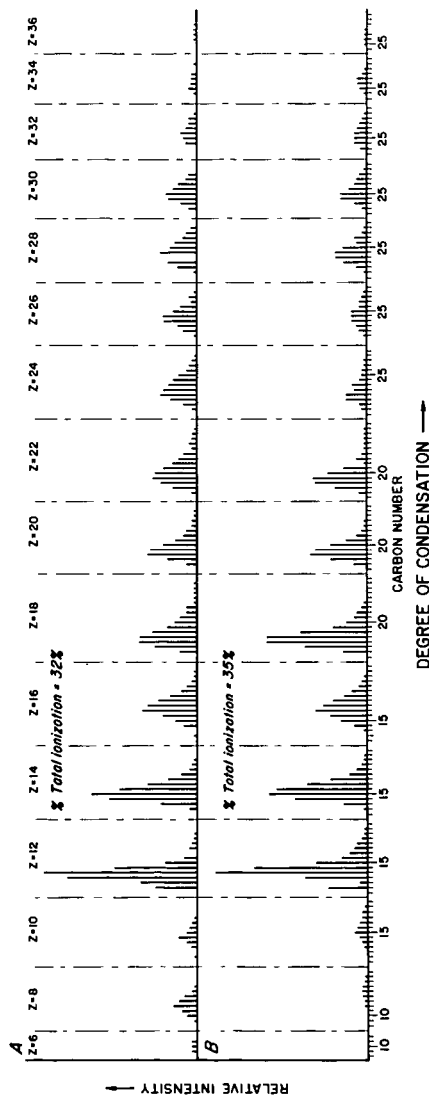   pressure)

Figure 2.   HRMS Comparison of CH Formulas
            Identified in Coal Extracts
            (A) Catalyzed (B) Uncatalyzed

75

COAL LIQUEFACTION AND HYDROGEN
UTILIZATION AT LOW TEMPERATURES

B.C. Bockrath, E.G. Illig,
D.H. Finseth, and R.F. Sprecher

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

The initial conversion of coal to material that may be extracted by polar solvents such as tetrahydrofuran or pyridine requires only relatively mild liquefaction conditions. The chemistry of the initial dissolution steps is very likely to be of great importance to the overall liquefaction process in that the yield and character of the initially formed products may greatly influence the success of subsequent liquefaction steps. Although conversion to the initial products seems to require a minimum of bond breaking, hydrogen-deuterium exchange reactions indicate that a rich chemistry transpires at the same time (1-4).

In the following experiments, the conversion of coal was examined as a function of several variables over the range of temperatures from 300°C to 450°C. The net change in both the content and the distribution of hydrogen among the products was followed using an analytical scheme based on elemental and NMR analyses. This method has been used to determine the net hydrogen utilization divided among categories for hydrogenation, hydrocarbon gas formation, heteroatom removal, and matrix bond breaking (5).

Experimental

Coal liquefaction was conducted in a 0.5-L stirred autoclave. In a typical experiment, 30 g (maf) of coal ground to pass 60 mesh was charged to the autoclave along with 70 g of coal-derived solvent. The solvent was a distillate cut (240°C-450°C) obtained from operations at the SRC-II pilot plant at Ft. Lewis, Wash. The autoclave was pressurized with the appropriate amount of hydrogen or nitrogen to obtain the desired operating pressure at temperature. Heat-up time to liquefaction temperatures was about 45 minutes. The autoclave was held at temperature for the specified time and then rapidly cooled by means of internal water-cooling coils. Grab samples of the off-gas were taken for analysis by gas chromatography as the autoclave was depressurized.

Conversion data in Figures 1 and 2 were obtained by first filtering the autoclave contents through a Whatman #541 filter on a Buchner funnel maintained at 60°C. The residue was then washed with tetrahydrofuran (THF) until the washings were nearly colorless. Data in Figure 3 were obtained by first digesting the liquid product from the autoclave with THF. The digest was vacuum-filtered through Whatman #2 filter paper, and the residue was washed with THF until the extract was nearly colorless. All residues were dried at 110°C and weighed. Conversion values were based on the weight of dried residue.

The methods used to determine hydrogen utilization data have been described (5). Data from the elemental analysis of the feed coal and liquefaction solvent, including the direct oxygen analysis, were used in these calculations (see Table 1). The liquid products were separated by Soxhlet extraction with methylene chloride. The carbon aromaticities were determined by ^{13}C NMR using CP/MAS techniques on the insoluble fraction and high resolution ^{13}C NMR in CD_2Cl_2 for the extract.

Results and Discussion

Liquefaction. The reactivities of the two bituminous coals are compared in Figure 1 as a function of temperature. The pronounced difference in reactivity at 325°C decreases rapidly with increasing liquefaction temperature. Although a difference in reactivity of these coals was expected, it is nonetheless remarkable that the conversion of the Illinois coal remains high even at a temperature as low as 325°C. The differences in patterns of hydrogen utilization discussed below are not striking for these two coals. The structural differences between the coals that are responsible for their individual responses to reaction temperature is a matter still open to question. At least, these data indicate that the choice of feedstock coal is even more critical for liquefaction at lower temperatures than at conventionally used temperatures.

The conversion of the Illinois coal is shown in Figure 2 as a function of reaction time after reaching temperature for three temperatures. It is evident that most conversion is complete within a short initial period of reaction even for the lowest of liquefaction temperatures. Undoubtly, some of this conversion occurs during heat-up. Although conversion to low molecular weight products may require more severe conditions, the breakdown of the matrix structure of coal requires little time at modest temperatures. This same pattern of reactivity was noted earlier for liquefaction of coal in tetralin at 400°C (6). The present experiments show that the "prompt" yield of extract increases somewhat with temperature.

The effect of hydrogen pressure on conversion is quite significant. Figure 3 contains conversion data obtained at various temperatures and pressures of hydrogen or nitrogen. As expected, conversions increase with hydrogen pressure but hardly change with increasing nitrogen pressure. The sensitivity of conversion to hydrogen pressure is a function of liquefaction temperature. For example, increasing hydrogen pressure from zero to 2000 psi produces a larger increase in conversion at 400°C than at 350°C. It is not known whether this difference is related to the thermochemistry of bond scission reactions or to the state of reduction of pyrite in the mineral matter to pyrrhotite, which may act as a modest catalyst for coal liquefaction. Under these reaction conditions, analysis of the off-gases for H_2S and of the recovered mineral residues for pyrrhotite content shows that the reduction of pyrite is incomplete at 350°C. It is somewhat greater at 400°C, but probably not yet complete.

The character of the liquefaction solvent is well-known to have a major influence on conversion under conventional conditions. A number of experiments were made to determine whether conversions obtained at the relatively low temperatures employed here would be sensitive to modifications in the coal-derived liquefaction solvent. In one case, 10% of the weight of the coal-derived solvent was replaced by tetralin, a well-known hydrogen donor. Many studies have shown that coal conversion increases with minor addition of tetralin to a liquefaction solvent that is poor in donable hydrogen (7). Conversions were not changed within experimental error for reaction temperatures of 325°C, 350°C, and 400°C under hydrogen pressures of either 1000 or 2000 psig. Thus the amount of conversion under these conditions is not limited by lack of hydrogen donor compounds in the coal-derived solvent.

In a similar way, 10% of the weight of the coal-derived solvent was replaced by pyrene, a compound reported to be especially effective as both a hydrogen transfer agent (8) and a physical solvent for promoting liquefaction (9). Addition of this compound also had no effect within experimental error on conversion obtained at 350°C or 400°C under 1000 psig hydrogen. Taken together, these experiments indicate that for liquefaction at relatively low temperatures, the coal-derived solvent employed is not lacking in components suited for hydrogen donation, hydrogen shuttling, or physical solvation.

77

Hydrogen Utilization. A second set of autoclave experiments was performed to determine if changes in hydrogen distribution during liquefaction were different for coals of different reactivity. For initial experiments, the reaction conditions selected were 2000 psi hydrogen and 15 min. at various temperatures. In order to improve the reliability of the hydrogen distribution data, the work-up procedure was modified to use only solvents compatible with the NMR measurements needed to monitor hydrogenation. The entire contents of the autoclave were Soxhlet-extracted with methylene chloride to yield soluble and insoluble fractions. The yield of soluble material is less using methylene chloride, but residual solvent does not interfere with subsequent NMR aromaticity measurements. Both the soluble and insoluble fractions undergo elemental and NMR analysis. Thus, the relative amount of each fraction does not affect the values determined for the net amount of hydrogen used. For both coals, the gas yield was negligible at 300°C and 350°C, but increased to 1.2%-1.5% at 400°C and 8.2%-8.4% at 450°C on an maf basis.

The total hydrogen utilization is divided into four categories in Table 2. These results are arrived at using an analytical approach described previously (5). Entries in Table 2 give the net number of hydrogens incorporated (positive sign) or produced (negative sign) per 100 carbons of feed slurry. It must be emphasized that these numbers indicate only net changes in hydrogen involved in a particular mode of utilization and they include all the carbon in the whole feed slurry not just that in the coal. Negative numbers appearing in Table 2 for hydrogenation and matrix bond cleavage indicate that hydrogen (not necessarily in the form of H_2 gas) is being generated within the slurry by dehydrogenation (aromatization) or condensation reactions, respectively.

The data in Table 2 indicate that cracking reactions producing C_1-C_4 hydrocarbon gases are not significant hydrogen consumers up to at least 400°C. Heteroatom removal increases with reaction temperature and is primarily oxygen removal under these conditions. (The maximum consumption by removal of N + S in these runs was 0.5 H/100 C for Illinois #6 at 450°C.) The higher content of labile oxygen of the Illinois #6 coal is reflected in Table 1.

The effect of temperature on the aromaticity of the total product (sols + insols + gases) is indicated in Figure 4. The trend to increasing product aromaticity with increasing temperature is the same for both coals. The data indicate that at low temperatures the net chemistry is hydrogenation, but above about 400° the total product aromaticity exceeds that of the feed slurry. This indicates that the net reaction above 400°C, even under 2000 psi hydrogen gas, is aromatization of the feed slurry (coal + solvent).

A similar pattern was observed in an earlier study of hydrogen utilization in a small continuous reactor, although in that case the magnitude of the variation of net hydrogenation with temperature was larger (5). This dominance of aromatization over hydrogenation at high temperatures is expected on thermodynamic grounds.

During liquefaction, bonds are being both broken (thermolysis) and formed (condensation). The category "matrix cleavage" in Table 2 attempts to quantitate the amount of hydrogen involved in bond-making/bond-breaking chemistry of the feed slurry. This value for the hydrogen involved in bond cleavage is necessarily determined by difference and thus should be interpreted with caution. With this warning it can be noted that for the Blacksville liquefaction experiments at 400°C and 450°C, the net hydrogen utilized in matrix cleavage is nil, indicating that any bond cleavage that occurs consuming hydrogen is balanced by condensation reactions producing hydrogen. At 325°C for the Blacksville coal, the data indicate net production of 2 hydrogens per 100 slurry carbons or a slight dominance of condensation reactions over thermolysis reactions. It is not unreasonable to expect condensation to predominate at low temperatures. The 325°C

78

experiments with Illinois #6 coal also indicate a predominance of condensation reactions, but the scatter of the data for the Illinois #6 coal liquefaction experiments is too high to comment on with confidence.

The net amount of hydrogen consumed in matrix cleavage is a measurement of the resultant of two opposing reaction routes and is thus expected to be a function of solvent type, reaction time, catalyst, coal, and temperature. The response of hydrogen utilization to these variables is now under investigation. The present data form a baseline for future comparisons. Improvements in the analytical method will make it easier to form firm conclusions on the relative importance of condensation versus thermolysis as a function of reaction conditions.

It is interesting to note, however, that both in this work ($325^{\circ}C$ data) and in the previous study of continuous unit operation, there is evidence for the dominance of condensation reactions under mild conditions. The analytical approach used to generate the data in Table 2 is still undergoing refinement, but it appears that it may be quite useful for characterizing differences in liquefaction chemistry and their dependence on reaction conditions.

REFERENCES

1. J.A. Franz, Fuel, 58, 405 (1979).

2. I.B. Goldberg, H.R. Crowe, J.J. Ratto, R.P. Skowronski, and L.A. Heredy, Fuel, 59, 133 (1980).

3. M.A. Wilson, P.J. Collin, P.F. Barron, and A.M. Vassallo, Fuel Processing Technology, 5, 281 (1982).

4. F.K. Schweighardt, B.C. Bockrath, R.A. Friedel, and H.L. Retcofsky, Anal. Chem., 48, 1254 (1976).

5. D.H. Finseth, B.C. Bockrath, D.L. Cillo, E.G. Illig, R.F. Sprecher, H.L. Retcofsky, and R.G. Lett, Am. Chem. Soc. Div. Fuel Chem. Preprints, 28(5), 17 (1983).

6. R.C. Neavel, Fuel, 55, 237 (1976).

7. B.C. Bockrath, in "Coal Science," (M.L. Gorbaty, J.W. Larsen, and I. Wender, Eds.) Vol. 2, pp. 65-124, Academic Press, NY (1983).

8. F.J. Derbyshire and D.D. Whitehurst, Fuel, 60, 655 (1981).

9. I. Mochida, A. Takerabe, and K. Takeshita, Fuel, 58, 17 (1979).

TABLE 1. ELEMENTAL ANALYSES, MAF

	C	H	N	O	S
BLACKSVILLE COAL	80.6	5.6	1.4	9.4	3.1
ILLINOIS #6 COAL	73.7	5.6	1.5	14.8	4.5
SOLVENT	87.1	8.0	1.4	3.0	0.4

MOISTURE FREE ASH CONTENTS WERE BLACKSVILLE = 11.9%, ILLINOIS #6 = 13.6%, SOLVENT < 0.1%.

TABLE 2.
HYDROGEN UTILIZATION VS. COAL REACTIVITY
AND TEMPERATURE: HYDROGENS INCORPORATED
PER 100 CARBONS OF FEED SLURRY

FATE OF HYDROGEN	BLACKSVILLE #2			ILLINOIS #6					
	325°	400°	450°	300°	300° Dup.	325°	400°	450°	450° Dup.
Gas Make	0	0	3	0	0	0	0	3	3
Heteroatom Removal	0	1	1	1	0	1	2	3	3
Hydrogenation	1	-2	-3	1	1	2	0	-3	-3
Matrix Cleavage	-2	0	0	0	+2	-2	+2	-1	0
TOTAL	-1	-1	+1	+2	+3	+1	+4	+2	+3

Figure 2 - Conversion of Illinois #6 (River King) Coal at 2000 psi hydrogen.

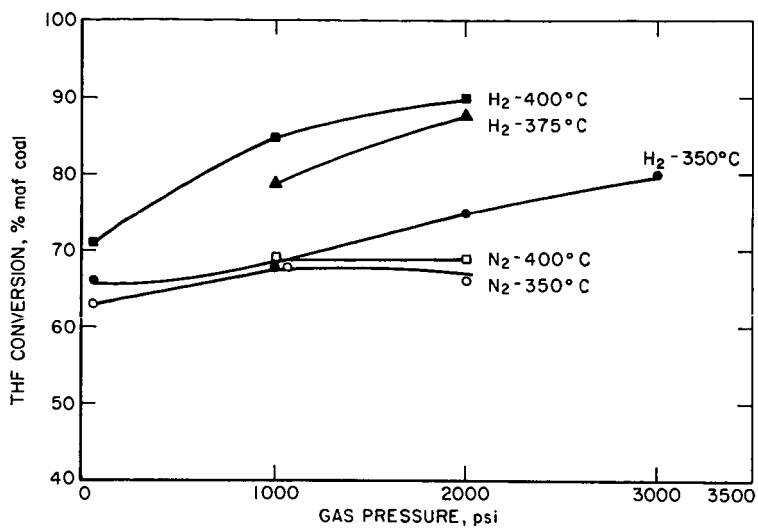Figure 1- Conversion of two coals versus temperature at 2000 psi hydrogen for 60 minutes.

81

Figure 3 - Pressure effect at various temperatures on Illinois #6 coal, 15 min at temperature.
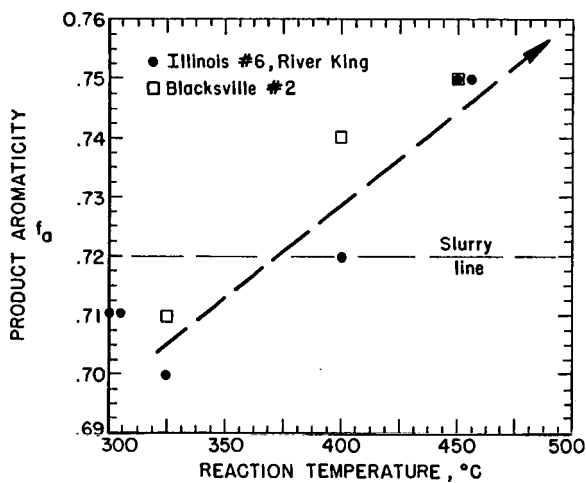

Figure 4. Product Aromaticity Versus Reaction Temperature for Blacksville #2 and Illinois #6

The Response of High Temperature Catalytic
Tetralin-Hydrogen Reaction to Free Radical Addition

W. M. Reed
A. R. Tarrer
J. A. Guin
C. W. Curtis
D. Garg

Auburn University
Department of Chemical Engineering
230 Ross Hall
Auburn University, AL   36849

I. INTRODUCTION

The literature is ambiguous regarding the reaction products obtained when tetralin and hydrogen are reacted above 425°C in the presence of a catalyst. Yen et al. (1) reported that tetralin disproportionation occurs, at 455°C, and naphthalene and only one of the decalin isomers are formed. They also reported the presence of an unidentified product. Hooper et al. (2), with the aid of recent advances in chromatographic analysis, suggested that the compound identified as a decalin isomer could be methyl indan and attempted to show that tetralin disproportionation did not occur. However, they did not analyze any actual products from catalytic hydrotreatment of tetralin.

In this report, gas chromatographic analyses of the products from catalytic dehydrogenation of tetralin at 450°C are presented. These analyses served as the baseline for comparison of reactions in which dibenzyl was added to provide a source of free radicals similar to those produced during the initial stages of coal liquefaction.

II. EXPERIMENTAL

The experiments were carried out in a tubing bomb microreactor constructed from a six inch length of 316 seamless stainless steel, 1/2-inch O.D. tubing. One end of the microreactor was sealed with a 1/2-inch Gyrolok cap. The other end was connected to a 3 and 1/4-inch length of 316 seamless stainless steel, 1/4-inch O.D., tubing with a Gyrolok reducing union. A Nupro fine metering valve was connected to the other end of the 1/4-inch O.D. tubing.

The reaction temperature was maintained by immersing the microreactor in a fluidized sand bath which was equipped with a temperature controller and a thermocouple for monitoring the temperature. The microreactor was agitated in a vertical plane with a 1 and 1/2-inch stroke. An agitation rate of 860 rpm has been shown (3) to reduce mass transfer effects in the microreactor. Two steel ball agitators of 1/8-inch diameter were also added to the microreactor to ensure good end-to-end mixing during reaction.

At the end of the desired reaction time, the microreactor was quenched in water (20-25°C) to stop the reaction. The microreactor was then vented and its contents collected in a vial.

The reaction products were analyzed using a Varian 3700 gas chromatograph equipped with a CDS-111 integrator. Separation was accomplished with a 60-meter, 0.314 mm I.D., fused silica capillary column with a DB-5 bonded phase (0.25 μm). To assist in the identification of the reaction products, some of the samples were analyzed with a gas chromatography-mass spectroscopy (GCMS) unit. A capillary column

was used for separation of the products. The composition of the other reaction experiments were then identified by comparison of the chromatograms with the chromatograms of the samples analyzed with GCMS.

III. RESULTS AND DISCUSSION

Three reaction parameters were chosen for manipulation to investigate the tetralin-hydrogen reaction at a relatively high temperature (450°C). These parameters were:

(1) addition of dibenzyl as a free radical precursor
(2) catalyst addition
(3) addition of gaseous hydrogen

Dibenzyl was selected as the free radical precursor. Dibenzyl cleaves at coal liquefaction conditions, producing benzyl free radicals. The primary reaction of dibenzyl is assumed to be thermal cracking followed by stabilization of the benzyl free radicals. Cronauer et al. (4) observed no increase in the rate of dibenzyl conversion with the addition of catalysts.   .

Table 1 presents the response of the product distribution to the addition of dibenzyl, and hence, the presence of free radicals. The principal products of the dibenzyl-tetralin-hydrogen reaction were benzene, toluene, methyl indan, and naphthalene. Very small amounts of ethyl benzene, butyl benzene, and trans-decalin were found in some experiments. Traces of cis-decalin and stilbene were also detected.

With the addition of dibenzyl, the most significant result was an increase in the formation of methyl indan, the isomer of tetralin. Approximately twenty percent of the tetralin was isomerized with the addition of dibenzyl, both with and without catalyst. Cronauer et al. (5) and McNeil et al. (6) have also reported an increase in the isomerization of tetralin with the addition of dibenzyl.

Even when there was no dibenzyl present, some isomerization of tetralin was observed (i.e., 5.7 wt% and 7.9 wt% methyl indan was formed with and without catalyst present, respectively). Isomerization of tetralin has been reported at temperatures as low as 350°C in a nitrogen atmosphere (2). Penninger and Slotboom (7,8) heated tetralin with hydrogen in the absence of catalyst at pressures of 10 to 100 atm and temperatures of 460 to 560°C. Methyl indan was reported among the principal products. They proposed that the dehydrogenation of tetralin to naphthalene provided the hydrogen atoms (i.e. free radicals) to initiate the isomerization reaction.

The formation of benzyl free radicals from dibenzyl is a thermal process. Thus, the use of catalysts was not intended to change the amount of dibenzyl converted; instead it was felt that its addition would alter the product distribution, i.e., mainly the relative amounts of tetralin isomerization and dehydrogenation products. The rate of formation of the tetralin isomer, methyl indan, changed slightly with the addition of presulfided CoMo/Al$_2$O$_3$ catalyst. However, the rate of tetralin dehydrogenation to from naphthalene increased significantly with the addition of catalyst. This increase was even more pronounced when no dibenzyl was added; the amount of naphthalene formation increased from 1.3 wt% to 13.0 wt% with the addition of catalyst. When dibenzyl was present, the amount of naphthalene formation increased only from 6.6 wt% to 9.8 wt% with the addition of catalyst.

For the product analyses given in Table 1, only a small amount of trans-decalin was observed, and that was when catalyst was present. No significant amount of cis-decalin was observed in any of the products analyzed. For the reaction

conditions used here then (450°C, etc.), catalyst addition caused an increase in the rate of dehydrogenation of the tetralin rather than an increase in that of hydrogenation.

The third reaction parameter which was studied was the addition of gaseous hydrogen. Vernon (9) has shown that molecular hydrogen can react directly with the benzyl free radical to yield toluene. Shah and Cronauer (10), however, have demonstrated that the benzyl free radicals have a distinct preference for combined hydrogen over molecular hydrogen under reaction conditions similar to those used in this work. They reported that this preference is enhanced if the concentration of hydroaromatics is high. The molecular hydrogen was believed to provide hydrogen for "rehydrogenation" of depleted hydrogen donor solvent. In this work, tetralin serves as the hydrogen donor, and a primary objective of the study was to evaluate the response of the rehydrogenation rate of the tetralin versus that of isomerization to the addition of gaseous hydrogen.

Two extremes of reactor atmosphere were used: a hydrogen atmosphere (800 psig at room temperature) and an inert nitrogen atmosphere (300 psig at room temperature). The product distributions for each case are presented in Table 2. The conversion of dibenzyl was approximately the same in each case. The rate of isomerization of tetralin to form methyl indan was lower in the nitrogen atmosphere. This result suggests that molecular hydrogen can participate in the reaction mechanism for tetralin isomerization. However, this participation may be indirect. In a hydrogen atmosphere the dehydrogenation rate for tetralin should be lower than that in a nitrogen atmosphere. As a result, more tetralin should be available for isomerization. A more direct role of the hydrogen could be that the benzyl radicals react with the molecular hydrogen to produce hydrogen atoms, then these atoms could participate directly in the tetralin isomerization reactions (8,9).

The rate of tetralin dehydrogenation was higher than that of isomerization with an inert nitrogen reaction atmosphere (Table 2). The opposite was true with a hydrogen atmosphere.

The reaction of tetralin in the presence of both dibenzyl and hydrogen was used as a baseline system for comparison. The increase in the amount of tetralin dehydrogenation that occurred, when no hydrogen was initially present, relative to that obtained with this baseline system was determined. The increase observed when no dibenzyl was present was also determined. These responses are compared in Table 3. Apparently the increase in the rate of tetralin dehydrogenation, in response to the absence of hydrogen, was much higher than it was in response to the absence of dibenzyl.

When no hydrogen was present there was about an 8.4 wt.% decrease from the baseline value (19.9 wt.%) in the amount of tetralin that isomerized to form methyl indan (Table 4). Similarly, when no dibenzyl was present, the amount of tetralin converted to methyl indan decreased by about 12.0 wt.% below the baseline value.

A number of compounds such as tetrahydroquinoline (THQ) have been shown to have a higher hydrogen donor reactivity than that of tetralin (12). A crude measure of the relative reactivity of the tetralin for donating hydrogen to the benzyl radicals was made by determining the decrease in the extent of tetralin dehydrogenation that occurred in response to the addition of either quinoline or phenanthridine. Quinoline and phenanthridine are basic nitrogen-containing aromatic compounds similar to those found in coal-derived liquids. These compounds have a relatively high adsorptivity. As a result, these compounds adsorb preferentially onto the catalyst surface and are hydrogenated in preference to compounds like naphthalene (i.e., the dehydrogenated tetralin product) which have a lower relative adsorptivity (13). The hydrogenated products of these compounds (eg. THQ) are excellent hydrogen donors.

McNeil et al. (6) measured the response of tetralin dehydrogenation and isomerization in the presence of dibenzyl to the addition of different polynuclear aromatic compounds (e.g. phenanthrene, pyrene). They observed an insignificant response to occur in the tetralin isomerization. However, a significant decrease in the tetralin dehydrogenation occurred in response to the addition of certain aromatics. In an earlier work (11), this decrease in tetralin dehydrogenation was observed to vary directly with the number of condensed rings in the aromatic compound added.

The response of tetralin isomerization to the addition of either quinoline or phenanthridine is shown in Figure 1. The presence of quinoline or phenanthridine had a significant influence on the extent of tetralin isomerization that occurred. However, as shown in Figure 2, the addition of either quinoline or phenanthridine caused only a slight decrease in the amount of tetralin dehydrogenation (14.2 wt.% versus 6.6 and 10.4 wt%). The relative insensitivity of the tetralin dehydrogenation to the addition of these basic nitrogen-containing compounds is somewhat surprising. Earlier it was shown that the presence of a catalyst caused a significant increase in tetralin dehydrogenation (Table 1). Preferential adsorption of the quinoline or phenanthridine on the catalyst should inhibit dehydrogenation. It appears, however, that these compounds act more to quench the benzyl radicals and thereby inhibit tetralin isomerization without significantly inhibiting dehydrogenation of the tetralin.

IV. SUMMARY OF RESULTS

The principal products of the high temperature, catalytic reaction of tetralin in the presence of dibenzyl and gaseous hydrogen were found to be naphthalene and methyl indan. A small amount of trans-decalin was observed to be formed. The isomerization of tetralin increased with the addition of dibenzyl, a free radical precursor. The addition of a presulfided CoMo/Al$_2$O$_3$ catalyst had a small effect on tetralin isomerization and dehydrogenation in the presence of dibenzyl. However, in the absence of dibenzyl, catalyst addition had a significant effect on tetralin dehydrogenation.

Tetralin dehydrogenation increased significantly when an inert nitrogen atmosphere rather than a hydrogen atmosphere was used.

Tetralin isomerization decreased significantly with the addition of either quinoline or phenanthridine; whereas tetralin dehydrogenation decreased only slightly with the addition of either of these compounds.

References
1. Yen, Y. K., Furlani, D. E., and Weller, S. W., Ind. Eng. Prod. Res. Dev., 15, 24 (1976).
2. Hooper, R. J., Battaerd, H. A., and Evans, D. G., Fuel, 58, 132 (1979).
3. Gallokato, S. V., "Analysis of Mass Transfer in Coal Liquefaction reactors," Ph.D. Dissertation, Auburn University, AL (March 1984).
4. Cronauer, D. C., Jewell, D. M., Shah, Y. T., and Modi, R. J., Ind. Eng. Chem. Fund., 18, 153 (1979).
5. Cronauer, D. C., Jewell, D. M., Shah, Y. T., and Kueser, K. A., Ind. Eng. Chem. Fund., 17, 291 (1978).
6. McNeil, R. I., Cronauer, D. C., and Young, D. C., Fuel, 62, 401 (1983).
7. Penninger, J. M. and Slotboom, H. W., Rec. Trav. Chim. Pays-Bas, 92, 513 (1973).
8. Penninger, J. M. and Slotboom, H. W., Rec. Trav. Chim. Pays-Bas., 92, 1089 (1973).
9. Vernon, L. W., Fuel, 59, 102 (1980).
10. Shah, Y. T. and Cronauer, D. C., Catal. Rev. - Sci. Eng., 20, 209 (1979).
11. Cronauer, D. C., McNeil, R. I., Young, D. C., and Ruberto, R. G., Fuel, 61, 610 (1982).
12. Curtis, C. W., Guin, J. A., and Kwon, K. C., "Coal Solvolysis in a Series of Model Compound Systems," Fuel, (in press).
13. Shridharani, K. G., "Mineral Catalysis of Oil-Producing Reactions in Coal Liquefaction," Ph.D. Dissertation, Auburn University, Auburn, Al., March 17, 1983.

Table 1

Response in Product Distribution to Addition of Dibenzyl,
with and without Catalyst Present

Initial Dibenzyl (wt%)	Catalyst (ppm)	Product Distribution, wt%					
		Tetralin	Naphthalene	Methyl Indan	Benzene	Toluene	Dibenzyl
0	0	92.9	1.3	5.7	--	--	--
20	0	56.9	6.6	16.4	0.6	11.4	8.0
0	1000	71.2	13.0	7.9	--	--	--
20	1000	54.3	9.8	15.9	0.6	10.4	8.8

Reaction Mixture: 5.0g dibenzyl and tetralin
Catalyst Loading: 1000 g of total metal in presulfided $CoMo/Al_2O_3$ per 10^6 g
                       of tetralin.
Reaction Conditions: Temperature   = 450°C
                       Initial H_2 Pressure = 800 psig at 25°C
                       Time   = 60 minutes
                       Agitation Rate   = 860 rpm
                       Reactor   = Tubing Bomb Microreactor

Table 2

Comparison Between Product Distribution in a Hydrogen Atmosphere
with That in a Nitrogen Atmosphere

Atmosphere	Product Distribution, Weight %					
	Tetralin	Naphthalene	Methyl Indan	Benzene	Toluene	Dibenzyl
H_2	54.3	9.8	15.9	0.6	10.4	8.8
N_2	47.0	23.6	9.2	0.3	9.8	9.8

Reaction Mixture: 5.0 g 20 wt% dibenzyl in tetralin
                    1000 g metal in presulfided $CoMo/Al_2O_3$ ctalyst per 10^6
                    of tetralin
Reaction Conditions: Temperature   = 450°C
                       Initial Pressure   = 800 psig H_2, or 300 psig N_2, at 25°C
                       Time   = 60 minutes
                       Agitation Rate   = 860 rpm
                       Reactor   = Tubing Bomb Microreactor

Table 3

Comparison Between the Change in the Weight Percent
of the Tetralin Dehydrogenated with No Dibenzyl
Present and That with No Hydrogen Gas Present

Change from Baseline Conditions*	Increase in Amount of Tetralin Dehydrogenated (ΔWt.%)
No Dibenzyl Present	0.7
No Hydrogen Present	17.5

*Baseline Reaction Conditions:
  Reaction Mixture: 5.0g of 20 wt.% dibenzyl in tetralin
  Catalyst Loading: 1000 g of total metal in presulfided CoMo/Al$_2$O$_3$ per
                       10^6 g of tetralin
Reaction Conditions: Temperature   = 450°C
                       Initial H$_2$ Pressure = 800 psig at 25°C
                       Time   = 60 minutes
                       Agitation Rate   = 860 rpm
                       Reactor   = Tubing Bomb Microreactor


Table 4

Comparison Between the Change in the Weight Percent
of the Tetralin Isomerized with No Dibenzyl
Present and That with No Hydrogen Gas Present

| Change from Baseline Conditions*	Decrease in Amount of Tetralin Isomerized (ΔWt.%)
No Dibenzyl Present	12.0
No Hydrogen Present	8.4

*Baseline Reaction Conditions:
  Reaction Mixture: 5.0g of 20 wt.% dibenzyl in tetralin
  Catalyst Loading: 1000 g of total metal in presulfided CoMo/Al$_2$O$_3$ per
                       10^6 g of tetralin
Reaction Conditions: Temperature   = 450°C
                       Initial H$_2$ Pressure = 800 psig at 25°C
                       Time   = 60 minutes
                       Agitation Rate   = 860 rpm
                       Reactor   = Tubing Bomb Microreactor

Mixture of Hydrogen Donor and Hydrogen Donor Precursor
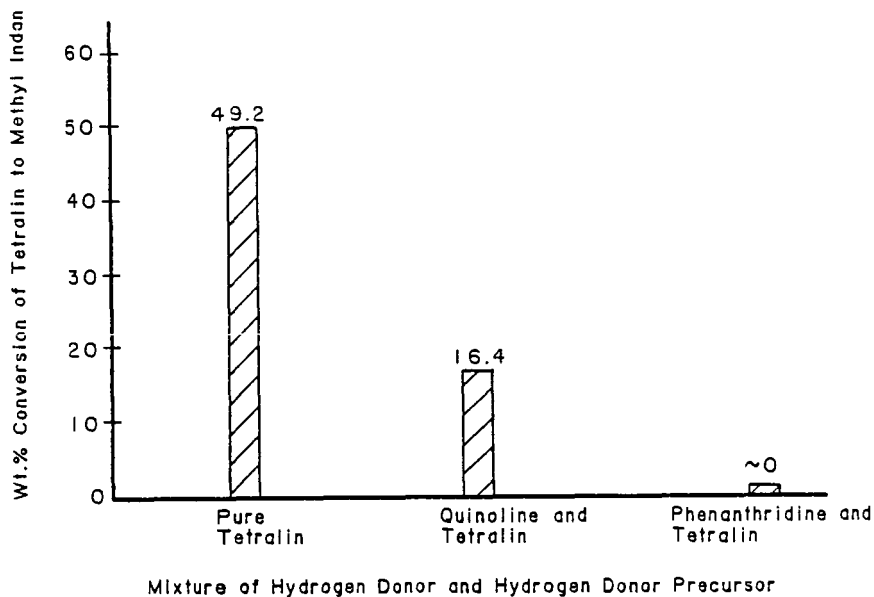
Reaction Mixture: 2.0 g 50 wt% dibenzyl in tetralin or 1:1 wt.
                    ratio of tetralin to quinoline or phenanthridine
                    1000 g of Mo per 10^6 g of tetralin and
                    quinoline or phenanthridine mixture

Reaction Conditions: Temperature   = 450°C
                      Initial H_2 Pressure = 800 psig at 25°C
                      Time   = 60 minutes
                      Agitation Rate   = 860 rpm
                      Reactor   = Tubing Bomb Micro-
                                            reactor

Figure 1. Response of Tetralin Isomerization to the addition of either
           Quinoline or Phenanthridine

Figure 2. Response of Tetralin Dehydrogenation to the addition of either Quinoline or Phenanthridine
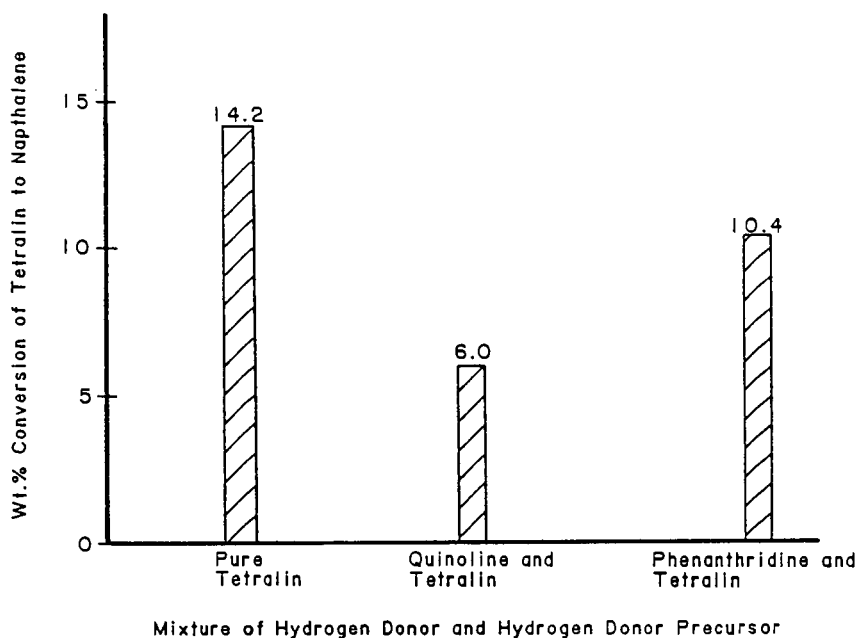
Reaction Mixture: 2.0 g 50 wt% dibenzyl in tetralin or 1:1 wt. ratio of tetralin to quinoline or phenanthridine 1000 g Mo per 10^6 g of tetralin and quinoline or phenanthridine mixture

Reaction Conditions:

Temperature	=	450°C
Initial H_2 Pressure	=	800 psig at 25°C
Time	=	60 minutes
Agitation Rate	=	860 rpm
Reactor	=	Tubing Bomb Micro-reactor